Atmospheric Environment 118 (2015) 87–97

Contents lists available at ScienceDirect

Atmospheric Environment

journal homepage: www.elsevier.com/locate/atmosenv

Variation of the ratio of nitrate to non-seasalt sulfate in precipitation over East Asia with emissions from China

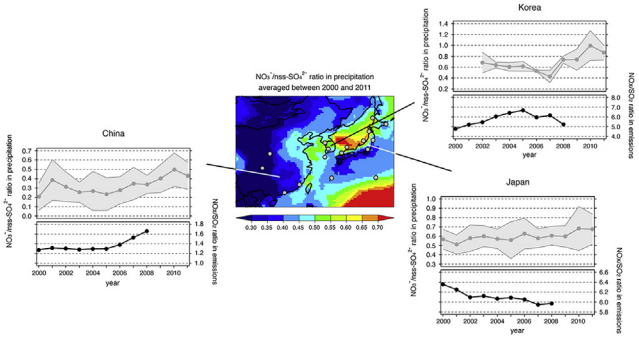
Syuichi Itahashi [a, *], Itsushi Uno [b], Hiroshi Hayami [a], Shin-ichi Fujita [a]

[a] Environmental Science Research Laboratory, Central Research Institute of Electric Power Industry, 1646 Abiko, Abiko, Chiba 270-1194, Japan
[b] Research Institute for Applied Mechanics, Kyushu University, 6-1 Kasuga Park, Kasuga, Fukuoka 816-8580, Japan

HIGHLIGHTS

- Ratio of nitrate to non-seasalt sulfate in precipitation was examined.
- Precipitation and its chemical composition are well simulated over East Asia.
- Ratio increased dramatically during 2006–2011 by 5–10%/year in East Asia.
- Increment of NOx emissions in China mainly increased the ratio in China.
- Decline of SO_2 emissions in China effected to ratio increases in Korea and Japan.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 15 April 2015
Received in revised form
21 July 2015
Accepted 23 July 2015
Available online 31 July 2015

Keywords:
Precipitation chemistry
Nitrate to non-seasalt sulfate ratio (NO_3^-/nss-SO_4^{2-})
NOx–SO_2 emission ratio (NOx/SO_2)
Community multi-scale air quality (CMAQ) model
East Asia

ABSTRACT

Changes in anthropogenic emissions in East Asia will cause substantial variations in the precipitation chemistry. In particular, the effects of changes in China, where NOx emissions have been rising continuously and SO_2 emissions peaked in 2005–2006, are important. The absolute chemical concentration in precipitation is inherently linked to the amount of precipitation; therefore, in this work we used the ratio of nitrate (NO_3^-) to non-seasalt sulfate ($\text{nss-}SO_4^{2-}$) concentration in precipitation on an equivalent basis (hereinafter, *Ratio*). Here, we extend the method in our previous study (Itahashi et al., 2014a) to Korea and China. We analyzed the long-term behavior of *Ratio* in precipitation during 2000–2011 and investigated the factors responsible for variations of *Ratio* in precipitation by using a model simulation with sensitivity analysis for emission changes in China. *Ratio* over Japan, Korea, and China decreased slightly or remained constant during 2000–2005 (first 6 years of 2000–2011) and subsequently increased during 2006–2011 (last 6 years of 2000–2011). Linear regression analysis of the observations showed significant increases in *Ratio* during 2006–2011: +3.4 ± 1.0%/year, +13.2 ± 4.1%/year, and +9.8 ± 2.5%/year for Japan, Korea, and China, respectively (each $p < 0.05$). These variations in *Ratio* corresponded closely to the changes in the NOx/SO_2 emission ratio in China. This suggests that anthropogenic emissions from China were responsible for most of the variation in precipitation chemistry in East Asia. Model simulations for 2000–2011 and their reproducibility were validated by comparison with the observation dataset, and they captured the observed features well. Sensitivity analysis of emissions from China in the model simulation for 2009–2011 clarified that the increase in NOx emissions from China contributed to 55–60% of the increase in *Ratio* in China and around 50–55% in Korea and Japan; the contribution of the increase in NOx emissions was smaller in the region downwind

* Corresponding author.
E-mail addresses: isyuichi@criepi.denken.or.jp (S. Itahashi), uno@riam.kyushu-u.ac.jp (I. Uno), haya@criepi.denken.or.jp (H. Hayami), fujiz@criepi.denken.or.jp (S.-i. Fujita).

http://dx.doi.org/10.1016/j.atmosenv.2015.07.032

of China. In contrast, the decline in SO_2 emissions from China contributed below 40% in China and around 40–45% in Japan; the effect was larger in the region downwind of China.

1. Introduction

Acid deposition began to be recognized as a regional-scale environmental problem in Europe and eastern North America during the 1970s (U.S. NAPAP, 1991). Recently, East Asia has begun to experience this problem (Fujita et al., 2000). Anthropogenic emissions in East Asia have been rising since 1980, as the population of East Asia has grown and the economies of East Asian countries have expanded. Emissions in Asia have surpassed the emissions in North America and Europe in the mid-1990s (Akimoto, 2003). Emissions are especially high in China, where NOx emissions have been rising steadily. However, fuel-gas desulfurization systems introduced as part of China's 11th Five-Year Plan (2006–2010) have meant that SO_2 emissions in China peaked in 2005–2006 and have subsequently declined (Kurokawa et al., 2013). The changes in anthropogenic emissions of acidifying pollutants in East Asia are expected to have a substantial effect on the precipitation chemistry over East Asia.

To understand the chemical composition of precipitation, the behavior of deposited chemicals that are generated in the atmosphere and precipitated out must be elucidated. However, the wet deposition itself would be affected by the amount of precipitation. For this reason, the ratio of nitrate (NO_3^-) concentration to non-seasalt sulfate ($nss\text{-}SO_4^{2-}$) concentration in precipitation on an equivalent basis, hereinafter referred to as *Ratio*, is useful for evaluating the relative contributions of nitrogen and sulfur to the acidity of precipitation. Although the difference in size distribution between NO_3^- and $nss\text{-}SO_4^{2-}$ affects their scavenging efficiency, and thus their concentration in precipitation, several studies have highlighted the link between *Ratio* and its related emissions. Over Japan, *Ratio* was about 0.41 between 1987 and 1990 (Fujita et al., 2003). For 1987–1996, over western Japan *Ratio* increased substantially by 0.09–0.17, reaching about 0.5 in the late 1990s. This corresponded to the larger increase in NOx emissions compared with SO_2 emissions across East Asia (Takahashi and Fujita, 2000). In our previous study (Itahashi et al., 2014a), we analyzed the long-term behavior of *Ratio* in precipitation over the Japanese archipelago for 2000–2011. This showed that *Ratio* remained constant around 0.5–0.6 between 2000 and 2005, and subsequently increased to 0.6–0.7 between 2006 and 2011. During this period, the NOx/SO_2 emission ratio in Japan has been constantly decreasing, and variations in *Ratio* closely followed the changes in the NOx/SO_2 emission ratio in China. This suggests that anthropogenic emissions from China were responsible for the change in precipitation chemistry over Japan. Sensitivity analysis in the model simulation demonstrated that the increase in NOx emissions from China and the decline in SO_2 emissions from China contributed almost equally to the increases in *Ratio* in precipitation over Japan.

In this work, we analyze the chemical components in precipitation above China and Korea further, and investigate the behavior of precipitation chemistry, focusing on *Ratio*. This paper is organized as follows. In Section 2, the observation dataset for precipitation in China, Korea, and Japan are analyzed, and the long-term behavior for the period 2000–2011 is examined. In Section 3, the framework of the model simulation is introduced and validated by comparing model simulation results with observational data. The model simulation was conducted during 2000–2008 and two sensitivity analyses were conducted based on fixed and estimated emissions from China for 2009, 2010, and 2011. The factors controlling the variations in *Ratio* are examined. Finally, our conclusions are presented in Section 4.

2. Observed trends in precipitation chemistry

The observation datasets for wet deposition provided by the Acid Deposition Monitoring Network in East Asia (EANET) program (http://www.eanet.asia/index.html) were mainly used in this study. In China, observations have been conducted over three areas in southern China (Chongqing, Zhuhai, and Xiamen) and one area in central China (Xi'an). Observations from each site in these areas are from 2000. In Korea, observations at Cheju and Kanghwa are available from 2000, and those at Imsil are available from 2001. Following our previous study (Itahashi et al., 2014a), the observation datasets at 10 monitoring sites in EANET were used. In addition, we use datasets from the atmospheric composition and deposition data at Ryori conducted by the Japan Meteorological Agency (JMA) under the Global Atmosphere Watch (GAW) program of the World Meteorological Organization, and the cooperative network for monitoring precipitation chemistry established by the Central Research Institute of Electric Power Industry (CRIEPI). The CRIEPI data were obtained at Komae near urban Tokyo, and Goto Island at the western edge of Japan. The data from Komae were used for 2000–2011, and the data from Goto were used for 2000–2003. Samples were collected by wet-only samplers at 10 day intervals at CRIEPI sites, and daily at the EANET and JMA observation sites, except for weekly collection at Banryu, event or weekly collection at Chongqing and Xi'an in 2000, and weekly collection at Imsil in 2001. Concentrations of NO_3^- and SO_4^{2-} in precipitation were determined by ion chromatography and qualified by ion balance and conductivity agreement. The completeness of the data was determined from precipitation coverage duration and total precipitation (EANET, 2000a,b). If the annual mean data did not satisfy the EANET criteria, the monthly mean data for the corresponding year were not used. From the EANET, JMA, and CRIEPI monthly mean datasets, $nss\text{-}SO_4^{2-}$ concentration was calculated from the conservative assumption that sodium (Na^+) is a seasalt tracer. The geographical locations of the observation sites are mapped in Fig. 1, and detailed information on the observation period, longitude, latitude, altitude, and site classification of each site is listed in Table 1.

In this study, to analyze the long-term behavior over the 12 years during the period of 2000–2011, outliers in the observation data were carefully examined. Monthly mean concentrations of NO_3^- and $nss\text{-}SO_4^{2-}$ in precipitation were analyzed by using the Smirnov–Grubbs' outlier test. In this method, one outlier was detected at a time, assuming that the most probable distribution was an approximately normal distribution. The hypothesis of no outliers is rejected if

$$G = \frac{\max_{i=1,\ldots,N} |C_i - \overline{C}|}{s} > \frac{N-1}{\sqrt{N}} \sqrt{\frac{t^2_{(\alpha/2N,\, N-2)}}{N-2+t^2_{(\alpha/2N,\, N-2)}}} \quad (1)$$

where $N, \overline{C},$ and s are the number, mean, and standard deviation of

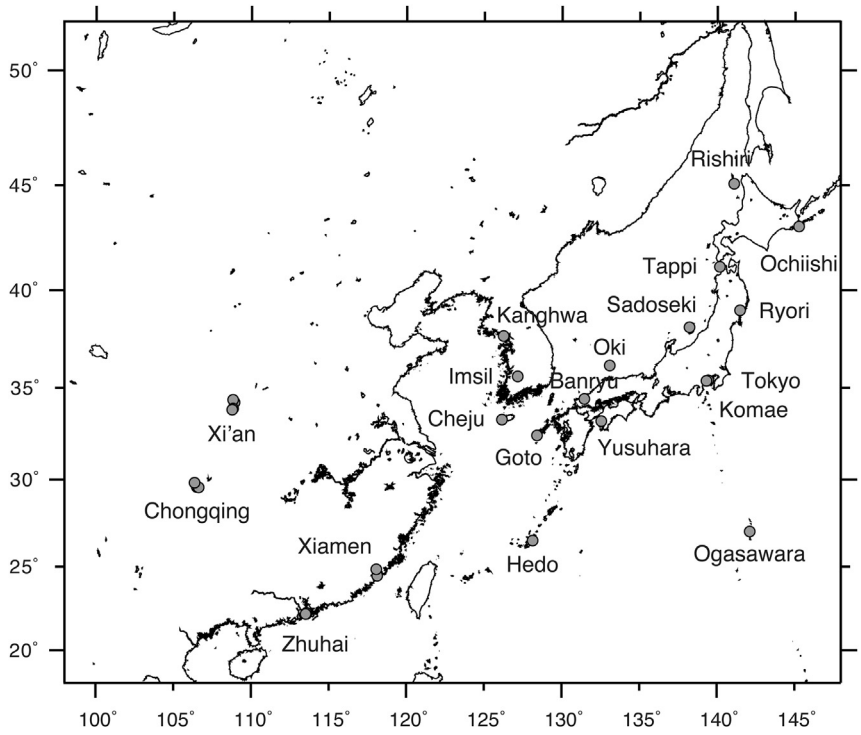


Fig. 1. Geographical mapping of observation sites used in this study. Detailed information about each observation site is provided in Table 1.

Table 1
Location of observation sites in China, Korea, and Japan.

Country	Site	Period	Latitude (°N)	Longitude (°E)	Elevation (m a.s.l.)	Classification
China	Chongqing					
	- Guanyinqiao	2000–2007	29.57	106.52	262	Urban
	- Haifu	2008–2011	29.62	106.50	317	Urban
	- Nanshan	2000	29.55	106.63	570	Rural
	- Jinyunshan	2001–2011	29.82	106.37	800	Rural
	Xi'an					
	- Shizhan	2000–2011	34.23	108.95	400	Urban
	- Weishuiyuan	2000–2006	34.37	108.85	366	Rural
	- Dabagou	2000	33.90	108.85	1200	Remote
	- Jiwozi	2001–2011	33.83	108.80	1800	Remote
	Xiamen					
	- Hongwen	2000–2011	24.47	118.13	50	Urban
	- Xiaoping	2000–2011	24.85	118.03	686	Remote
	Zhuhai					
	- Xiang Zhou	2000–2011	22.27	113.57	40	Urban
	- Zhuxian Cavern	2000–2006	22.20	113.52	45	Urban
	- Zhuxiandong	2007–2011	22.20	113.52	45	Urban
Korea	Cheju	2000–2011	33.30	126.17	72	Remote
	Kanghwa	2000–2011	37.70	126.28	150	Rural
	Imsil	2001–2011	35.60	127.18	–	Urban
Japan	Hedo	2000–2011	26.87	128.25	60	Remote
	Goto[b]	2000–2003	32.75	128.68	80	–
	Banryu	2000–2011	34.68	131.80	53	Urban
	Yusuhara	2000–2011	33.38	132.94	790	Remote
	Oki	2000–2011	36.29	133.19	90	Remote
	Sadoseki	2000–2011	38.25	138.40	136	Remote
	Komae[b]	2000–2011	35.64	139.58	27	–
	Tokyo	2007–2011	35.69	139.76	26	Urban
	Tappi	2000–2011	41.25	140.35	106	Remote
	Rishiri	2000–2011	45.12	141.21	40	Remote
	Ryori[a]	2000–2011	39.03	141.82	260	–
	Ogasawara	2000–2011	27.09	142.22	230	Remote
	Ochiishi	2003–2011	43.16	145.50	49	Remote

[a] JMA.
[b] CRIEPI, others with no remark: EANET.

concentrations of NO_3^- or nss-SO_4^{2-} in precipitation (C_i). $t^2_{(\alpha/2N,N-2)}$ denotes the critical value of the t-distribution with $(N-2)$ degrees of freedom and a significance level of $(\alpha/2\ N)$. Iterations were repeated until the dataset satisfied the specified significance level of 0.05. In this procedure, for Japan, Korea, and China, NO_3^- concentrations in precipitation were discarded at 2.8%, 4.6%, and 4.0%, respectively, and nss-SO_4^{2-} concentrations in precipitation were discarded at 1.5%, 3.4%, and 4.3%, respectively. Next, the annual mean precipitation amount and wet deposition of NO_3^- and nss-SO_4^{2-} were calculated from the monthly mean data if at least 9 months of data were available for a given year. After removing the outliers for NO_3^- and nss-SO_4^{2-} concentrations in precipitation, *Ratio* was calculated on a monthly basis. For the precipitation amount, months discarded by Grubb's test for NO_3^- and nss-SO_4^{2-} concentrations in precipitation were not used to maintain consistency in discarding concentrations.

Fig. 2 shows the long-term trend related to the precipitation chemistry of observations for 2000–2011. We used the statistical test for observations; therefore, the results for Japan were also presented. The observed precipitation was around 1000 mm/year in Korea and around 1500 mm/year in China and Japan (Fig. 2(a)). NO_3^- concentration in precipitation was in the decreasing order China, Korea, Japan. NO_3^- concentration in China was near 50 μeq/L, and that in Korea was 40 μeq/L; around twice that in Japan of 15–20 μeq/L (Fig. 2(b)). Fig. 2(e) shows that NOx emissions in China exhibited a consistent expansion, and this increase was more than twofold between 2000 and 2010 obtained by analyzing satellite observations (Itahashi et al., 2014b). However, NO_3^- concentration in precipitation above China did not increase; it leveled off near 50 μeq/L. In addition, the trends in NO_3^- concentration in precipitation above Korea and Japan were not consistent with the NOx emissions of each country. Nss-SO_4^{2-} concentration in precipitation was also in the decreasing order China, Korea, Japan, the same as for NO_3^- concentration in precipitation. The nss-SO_4^{2-} concentration in precipitation above China (200–400 μeq/L) was almost an order of magnitude larger than that above Japan (20–30 μeq/L), and that above Korea (60 μeq/L) was almost twice that in Japan (Fig. 2(c)). SO_2 emissions from China reached a peak in 2005–2006 (Fig. 2(e)). Partly because of the variations in SO_2 emissions, nss-SO_4^{2-} concentration in precipitation above China showed a high concentration of around 400 μeq/L in 2006, and then subsequently declined from 2007 to 2011 to around 200 μeq/L (Fig. 2(c)). However, high nss-SO_4^{2-} concentration in precipitation in 2000 could not be explained by SO_2 emissions alone. Variations in SO_2 emissions from Korea and Japan were constant or declined between 2000 and 2008, and nss-SO_4^{2-} concentration in precipitation above Korea and Japan did not exhibit a clear relationship with the SO_2 emissions. Relatively high nss-SO_4^{2-} concentrations in precipitation in Japan during 2000–2002 was partly caused by the SO_2 emissions from Miyakejima volcano in 2000 (Itahashi et al., 2014a). Except for this peak in Japan, nss-SO_4^{2-} concentrations in precipitation above Korea and Japan were high during 2005–2007, which might be connected to the variations in SO_2 emissions from China. Therefore, there were no clear temporal variations in NO_3^- and nss-SO_4^{2-} concentrations in precipitation above China, Korea, and Japan, as expected from the changes in emissions.

The changes in precipitation and NO_3^- and nss-SO_4^{2-} concentrations in precipitation did not provide useful information for 2000–2011 above China, Korea, and Japan; therefore, we focus on *Ratio* as a useful index (Fig. 2(d)). The long-term trends in *Ratio* are analyzed for the period 2000–2005 (first six years of 2000–2011), and for 2006–2011 (last six years of 2000–2011). As we reported in our previous study (Itahashi et al., 2014a), *Ratio* in Japan was 0.5–0.6 during 2000–2005, and increased to 0.6–0.7 during 2006–2011. The linear regression analysis for observed *Ratio* in Japan showed a constant trend (+1.1 ± 1.3%/year, no significant difference by Student's t-test) during 2000–2005 and a significant increase (+3.4 ± 1.0%/year, $p < 0.05$ by Student's t-test) during 2006–2011. The slight difference from our previous study (Itahashi et al., 2014a) stemmed from the outlier test used in this study. Compared with the behavior of *Ratio* above Japan, *Ratio* over China and Korea showed a more drastic increase during 2006–2011. Because of the data restriction by significance tests, *Ratio* in Korea during 2000 and 2001 was not used. *Ratio* in Korea increased from near 0.5 to around 1.0 during 2006–2011, and the linear regression analysis for observed *Ratio* in Korea showed a large, significant increase (+13.2 ± 4.1%/year, $p < 0.05$ by Student's t-test) during 2006–2011. Above Korea, a simultaneous dip in NO_3^- concentration in precipitation and peak in nss-SO_4^{2-} concentration in precipitation for 2007 was found, and this led to the abrupt decrease of *Ratio* in 2007. *Ratio* in China was 0.2–0.4 during 2000–2005, and increased to 0.5 during 2006–2011. The relatively small value of *Ratio* in China compared with those in Korea and Japan is caused by the relatively large concentration of nss-SO_4^{2-} in precipitation in China. The linear regression analysis for observed *Ratio* in China showed a non-significant decrease (−7.1 ± 3.7%/year) during 2000–2005 and a large, significant increase (+9.8 ± 2.5%/year, $p < 0.05$ by Student's t-test) during 2006–2011. To summarize the observation dataset, *Ratio* in East Asia decreased or remained constant during 2000–2005 and subsequently increased dramatically during 2006–2011.

The amount of NOx and SO_2 emissions (Kurokawa et al., 2013) and the NOx/SO_2 mole ratios in anthropogenic emissions from China, Korea, and Japan are shown in Fig. 2(e). The emission ratios for Korea and Japan were in the range of 5–6, which is much larger than that of China because the magnitudes of the relations between NOx and SO_2 emissions were different. The NOx/SO_2 emission ratio for Korea formed a sharp peak and that for Japan was a constant decrease. These changes in the NOx/SO_2 emission ratio were quite different from the variations in *Ratio* for precipitation for the same country. In contrast to the trends in NOx/SO_2 emission ratio in Korea and Japan, the emission ratio of NOx/SO_2 in China was almost constant (approximately 1.3) from 2000 to 2005, and then it linearly increased to 1.7 in 2008. This large variability in the NOx/SO_2 emission ratio in China was caused by the increase in NOx emissions and decline in SO_2 emissions after 2005. This variation in the emission ratio of NOx/SO_2 in China corresponded remarkably well to the variations in *Ratio* in precipitation above China, Korea, and Japan. These results clearly indicate the large effect that Chinese emissions have on precipitation chemistry over East Asia. To evaluate the effects of emission changes in China on precipitation chemistry further, especially on the behavior of *Ratio*, model simulations were conducted, and the results are discussed in the next section.

3. Investigation of factors that increase *ratio* over East Asia by numerical model

3.1. Model description

Model simulations over East Asia were conducted with the regional chemical transport model of the Community Multi-scale Air Quality (CMAQ) modeling system version 4.7.1 (Byun and Schere, 2006). The configuration of model is the same as in our previous study (Itahashi et al., 2014a); hence, we only describe it here briefly. The model domain covers all of East Asia with an 80 km horizontal grid resolution with a 98 × 78 grid, and a vertical grid on sigma-pressure coordinates extended to 50 hPa with 37 layers. The years 2000–2010 were simulated in our previous work (Itahashi

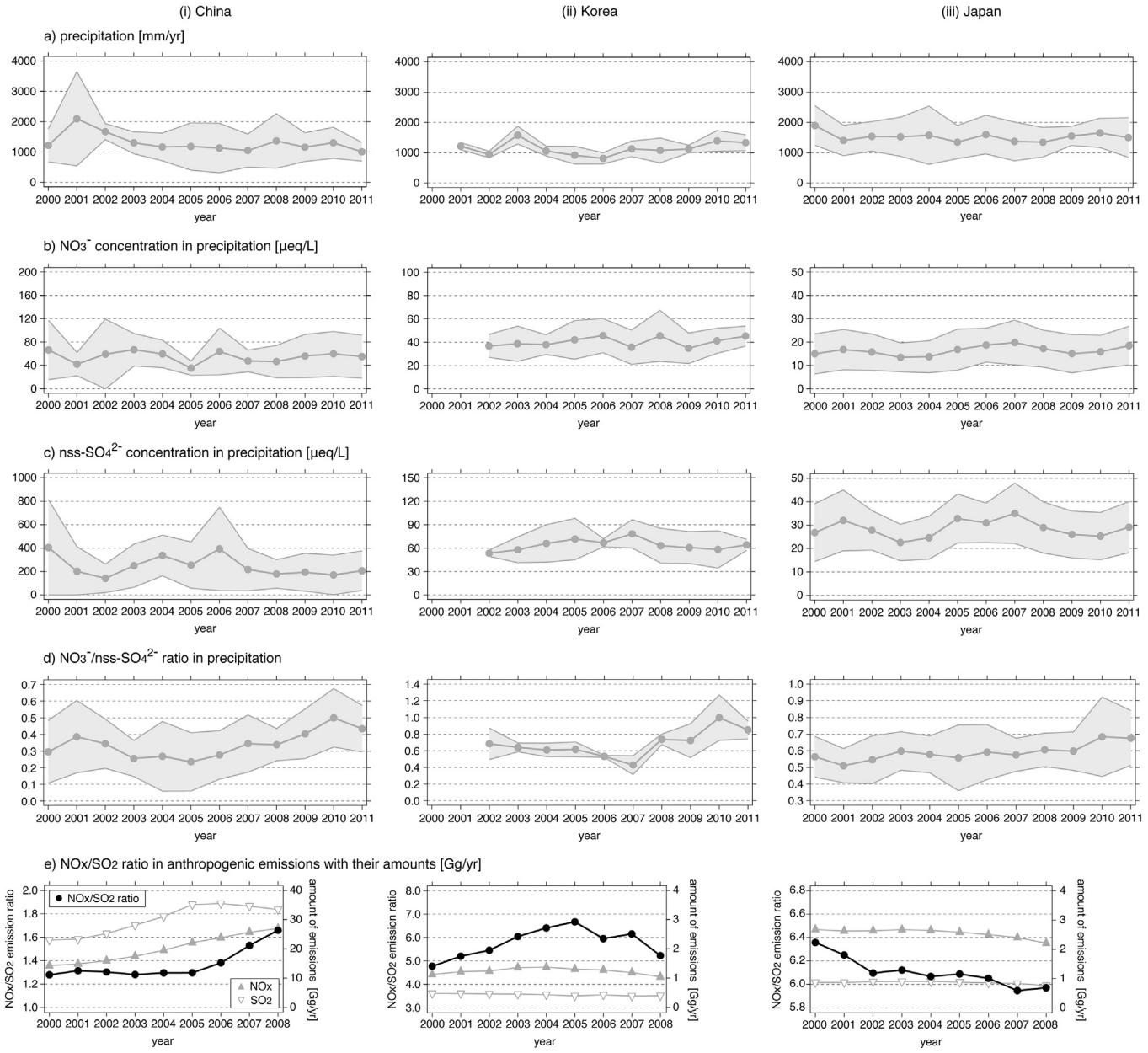


Fig. 2. Temporal variation in annual mean of (a) precipitation, (b) NO_3^- concentration in precipitation, (c) nss-SO_4^{2-} concentration in precipitation, (d) NO_3^-/nss-SO_4^{2-} ratio in precipitation for 2000–2011, and (e) NOx/SO_2 ratio in anthropogenic emissions and amounts for 2000–2008 observed above (i) China, (ii) Korea, and (iii) Japan. The mean values and standard deviations are denoted by the thick line with closed circles and shaded areas, respectively.

et al., 2014a), and we conducted additional calculations for 2011; each year was calculated with a 1 month model spin-up from the previous year.

Anthropogenic emissions and natural sources of NOx from soil were obtained from the latest Regional Emission inventory in ASia (REAS) version 2.1 (Kurokawa et al., 2013). REAS version 2.1 covers the years from 2000 to 2008. Therefore, two sensitivity simulations were prepared to investigate the controlling factors in the changes in chemical composition of precipitation during 2009 and 2011. The setups for the two sensitivity simulations were as follows: 1) the model simulation with anthropogenic emissions in 2009–2011 from China were fixed at the 2008 level (fixed emissions case), and 2) the model simulation with estimated emissions in 2009–2011 for NOx and SO_2 (estimated emissions case). These estimates were set based on the inverse estimation with the constraint of the satellite observations; the details of the estimation method are presented in Itahashi et al. (2014b) for NOx and in Itahashi et al. (2012) for SO_2. The anthropogenic NOx emissions from China were set at 27.2 Tg/year for 2009, 29.6 Tg/year for 2010, and 32.9 Tg/year for 2011; and the anthropogenic SO_2 emissions from China were set at 30.5 Tg/year for 2009, 27.7 Tg/year for 2010, and the same levels as 2010 for 2011. Note that the change in the spatial distribution was not considered in this emission estimation, only the total amount of NOx and SO_2 emissions was adjusted. Other emission sources (biogenic and biomass burning) used corresponding inventories for 2009, 2010, and 2011 in the sensitivity simulation, because our focus was the effect of anthropogenic emissions.

3.2. Evaluation of modeling reproducibility

The modeling reproducibility of the amount of precipitation,

NO_3^- and nss-SO_4^{2-} concentration in precipitation, and *Ratio* in precipitation determined by comparing observational data across Japan has been already reported (Itahashi et al., 2014a). The analysis period was extended in this study to 2011, and the Smilnov–Grubbs test was used to analyze long-term variation in the 12 years between 2000 and 2011. We present the validation of modeling reproducibility over Japan again and those for over China and Korea. Fig. 3 shows the amount of precipitation, NO_3^- and nss-SO_4^{2-} concentration in precipitation, and *Ratio* in precipitation as a scatterplot on logarithmic scales. Each data point on the plot corresponds to an annual mean for a site. These data are plotted for 2000–2011, and model simulation results are taken from the estimated emissions. For reference, 1:1, 1:2, and 1:3 lines are also inserted in Fig. 3. Tables 2–5 list the statistical analysis of model validity for precipitation amount, NO_3^- concentration in precipitation, nss-SO_4^{2-} concentration in precipitation, and *Ratio*, respectively. For precipitation, the model underestimated the observed precipitation amount although it performed acceptably, with normalized mean bias and error of 27–50%. The model simulation underpredicted the precipitation amount in China rather than in Korea and Japan. The correlation between the observations and the model simulation was better for China and Korea than for Japan. Student's t-test showed that these correlations are statistically significant ($p < 0.001$). The skill scores, which account for correlation and standard deviations of the two datasets, were around 0.7. For NO_3^- and nss-SO_4^{2-} concentration in precipitation, 70–99% of the model results and observations corresponded within a factor of 2 (Tables 3 and 4). The model results exhibited a moderate correlation (0.4–0.5) in China, and a strong correlation (0.7–0.8) in Korea and Japan. The modeling system can generally capture the observations over East Asia with a statistical significance level of $p < 0.001$. The modeling reproducibility for NO_3^- and nss-SO_4^{2-} concentrations in precipitation would partly stem from the underprediction of precipitation. Overall, our modeling system handled the observed features of the precipitation and concentrations of NO_3^- and nss-SO_4^{2-} in precipitation over East Asia well compared with more than 200 annual-mean ground-based observation datasets for 2000–2011.

In addition to the reproducibility of precipitation and chemical components in precipitation over East Asia, our modeling system can reproduce *Ratio* with more than 79% of results agreeing within a factor of 2, and more than 97% of results agreeing within a factor of 3 (Table 5). Skill scores in China, Korea, and Japan were around 0.7, which implies a good correlation considering standard deviations. The normalized mean bias is below 20%, and the normalized mean error is 25–40%. It is generally recognized that the meteorological model has some difficulty reproducing precipitation, which causes difficulty in capturing the chemical

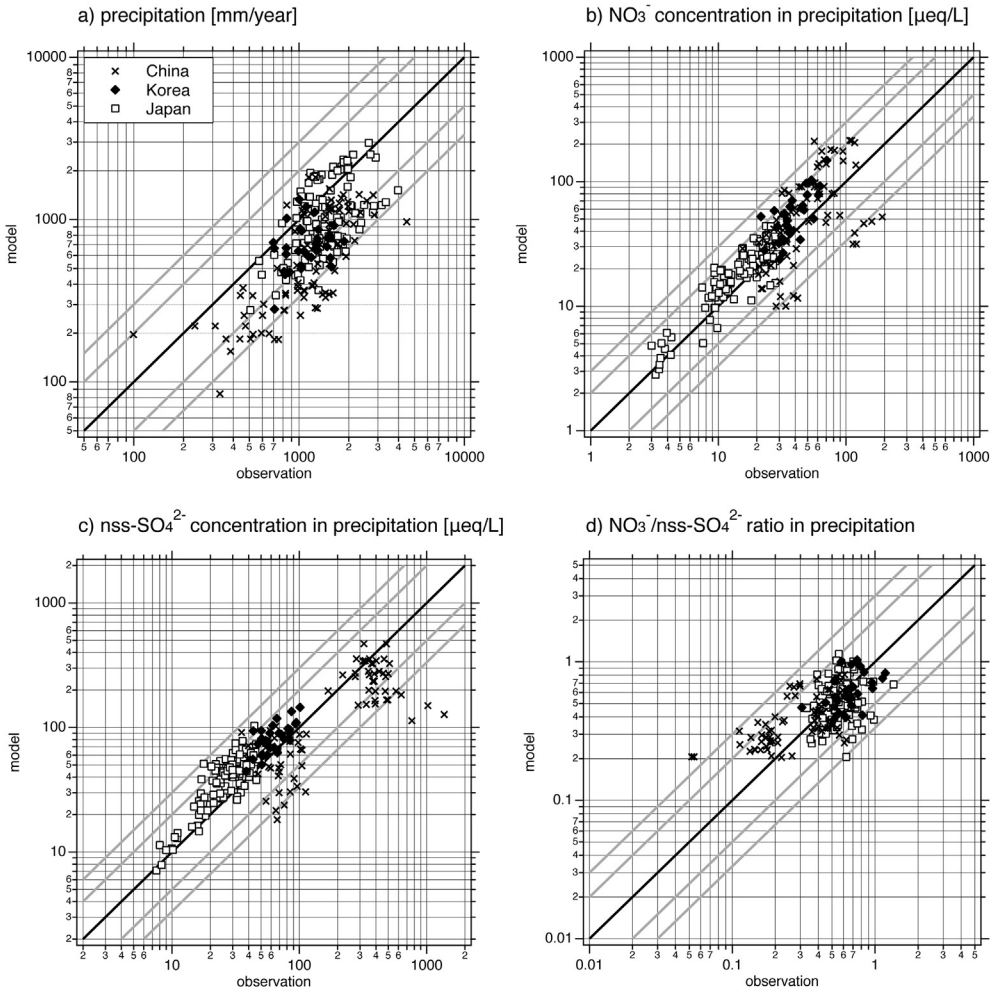


Fig. 3. Scatterplot of the annual mean observation (x-axis) and model simulation (y-axis) at each site in China (cross), Korea (diamond), and Japan (square) for (a) precipitation amount, (b) NO_3^- concentration in precipitation, (c) nss-SO_4^{2-} concentration in precipitation, and (d) NO_3^-/nss-SO_4^{2-} ratio in precipitation for 2000–2011. Model simulations are taken from the results of the estimated case. Reference lines are provided at ratios 1:1, 1:2, and 1:3.

Table 2
Statistical comparison of observations and model simulations for precipitation amount for 2000–2011.

Statistical quantity		China	Korea	Japan
Number of data		91	32	118
Mean (mm/year)	Observation	1273.8	1141.8	1515.7
	Model	678.6	714.1	1101.2
Standard deviation (mm/year)	Observation	673.3	299.0	584.5
	Model	440.9	220.8	566.9
Slope		0.40	0.13	0.45
Intercept		163.9	566.9	412.7
Correlation coefficient		0.62	0.63	0.47
Significance level by student's t-test		<0.001	<0.001	<0.001
Skill score		0.68	0.65	0.73
Normalized mean bias (%)		−46.7	−37.5	−27.4
Normalized mean error (%)		49.9	40.9	38.0
Root mean square error (mm/year)		797.3	546.0	724.2
Predictions within a factor of 2 of observations (%)		48.4	75.0	72.9
Predictions within a factor of 3 of observations (%)		79.1	96.9	98.3

Table 3
Statistical comparison of observations and model simulations for NO_3^- in precipitation for 2000–2011.

Statistical quantity		China	Korea	Japan
Number of data		77	29	108
Mean (μeq/L)	Observation	55.3	40.5	16.5
	Model	68.4	59.1	20.9
Standard deviation (μeq/L)	Observation	35.4	12.1	7.8
	Model	54.9	27.6	10.4
Slope		0.70	1.81	1.12
Intercept		29.6	−13.9	2.3
Correlation coefficient		0.45	0.79	0.84
Significance level by student's t-test		<0.001	<0.001	<0.001
Skill score		0.60	0.49	0.85
Normalized mean bias (%)		23.5	46.1	26.7
Normalized mean error (%)		64.7	50.6	33.9
Root mean square error (μeq/L)		51.8	27.0	7.2
Predictions within a factor of 2 of observations (%)		70.1	89.7	99.1
Predictions within a factor of 3 of observations (%)		88.3	100.0	100.0

Note: Model simulations for 2009–2011 are taken from the sensitivity simulation of estimated case.

Table 4
Statistical comparison of observations and model simulations for nss-SO_4^{2-} in precipitation for 2000–2011.

Statistical quantity		China	Korea	Japan
Number of data		80	29	109
Mean (μeq/L)	Observation	251.8	64.4	28.6
	Model	155.9	84.3	41.5
Standard deviation (μeq/L)	Observation	236.0	16.8	10.5
	Model	117.1	23.5	17.5
Slope		0.26	1.01	1.29
Intercept		89.9	19.1	4.7
Correlation coefficient		0.53	0.72	0.77
Significance level by student's t-test		<0.001	<0.001	<0.001
Skill score		0.49	0.77	0.70
Normalized mean bias (%)		−38.1	30.9	45.5
Normalized mean error (%)		44.4	32.0	47.5
Root mean square error (μeq/L)		222.3	25.7	17.4
Predictions within a factor of 2 of observations (%)		71.3	96.6	88.1
Predictions within a factor of 3 of observations (%)		90.0	100.0	100.0

Note: Model simulations for 2009–2011 are taken from the sensitivity simulation of the estimated case.

concentration in precipitation with air quality models. This problem can be avoided by using *Ratio*, which is another advantage of using *Ratio* for model simulations. Our modeling system also captured *Ratio* in precipitation, which was used in this study to evaluate the substantial changes in precipitation over East Asia.

The modeled spatial distribution of the precipitation amount, the chemical components in precipitation, and *Ratio* over East Asia averaged between 2000 and 2011 are plotted in Fig. 4. The annual mean precipitation over East Asia shows a clear geographical dependence on latitude; a high amount of precipitation (>3000 mm/year) over the Pacific Ocean, and a low amount of precipitation (<500 mm/year), especially over northern China. A high concentration of the chemical components in precipitation is found over northern China and decreases toward the east on the half-level (Korea and western Japan) and on the quarter-level (eastern Japan and Pacific Ocean). The spatial distribution patterns of NO_3^- and nss-SO_4^{2-} concentration in precipitation are similar, although the differences are clear in the analysis of *Ratio* in

Table 5
Statistical comparison between observations and model simulations for NO_3^-/nss-SO_4^{2-} ratio in precipitation for 2000–2011.

Statistical quantity		China	Korea	Japan
Number of data points		75	29	105
Mean	Observation	0.34	0.68	0.60
	Model	0.39	0.64	0.57
Standard deviation	Observation	0.17	0.19	0.15
	Model	0.16	0.19	0.19
Slope		0.51	0.40	0.44
Intercept		0.2	0.3	0.3
Correlation coefficient		0.53	0.40	0.37
Significance level by student's t-test		<0.001	<0.05	<0.001
Skill score		0.76	0.70	0.65
Normalized mean bias (%)		17.9	−6.8	−5.2
Normalized mean error (%)		40.4	25.0	30.7
Root mean square error		0.17	0.21	0.22
Predictions within a factor of 2 of observations (%)		78.7	100.0	91.4
Predictions within a factor of 3 of observations (%)		97.3	100.0	99.0

Note: Model simulations for 2009–2011 are taken from the sensitivity simulation of the estimated case.

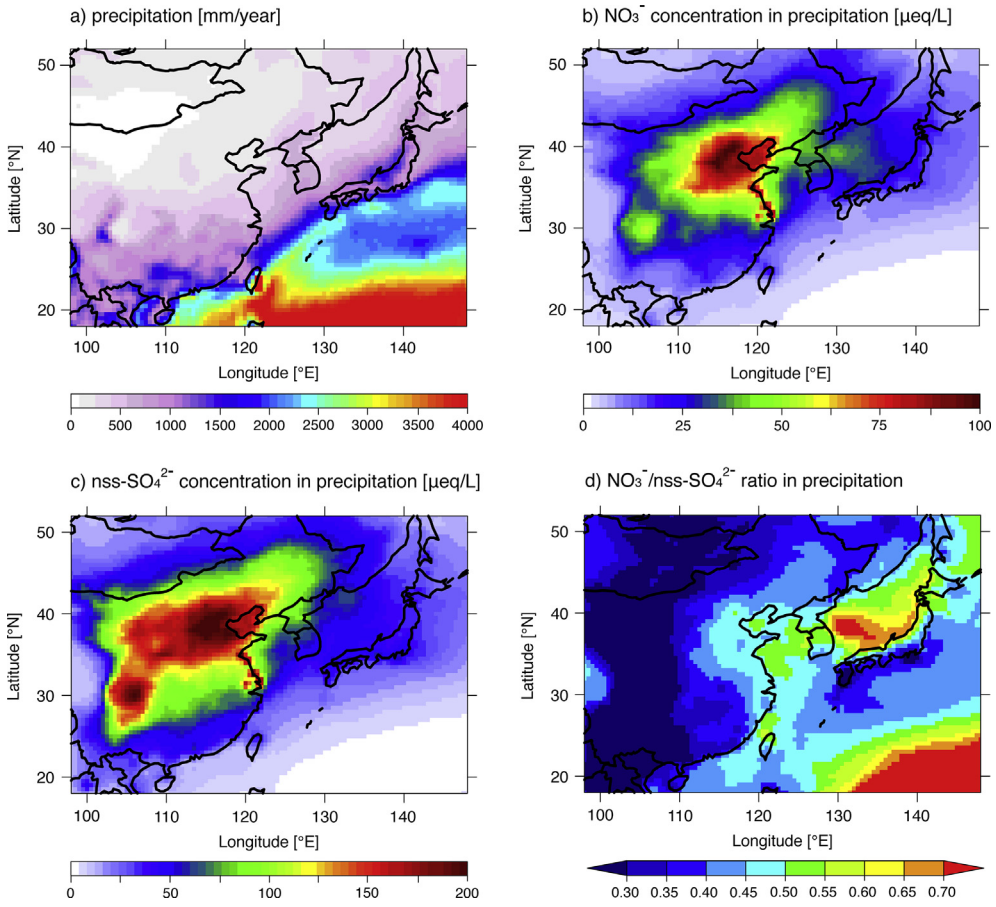


Fig. 4. Spatial distribution of modeled (a) precipitation amount, (b) NO_3^- concentration in precipitation, (c) nss-SO_4^{2-} concentration in precipitation, and (d) NO_3^-/nss-SO_4^{2-} ratio in precipitation averaged over 2000–2011.

precipitation. *Ratio* over East Asia during 2000–2011 varies at different locations. Above western China, the higher concentration of nss-SO_4^{2-} compared with that of NO_3^-, *Ratio* is below 0.3. However, in eastern China along the coastline and above Korea, *Ratio* is near 0.5, which means the molar quantities of nss-SO_4^{2-} and NO_3^- concentration are the same. The behavior of *Ratio* over Japan was more complex. On the one hand, for western to eastern Japan and the coastline of the Sea of Japan, *Ratio* is near 0.6, and *Ratio* is greater than 0.7 over eastern Korea to the Sea of Japan. On the other hand, for western to central Japan and the coastline of Pacific Ocean, *Ratio* is near 0.4. This is mainly caused by the large eruption of Miyakejima volcano in 2000 (Itahashi et al., 2014a). The geographical variation of *Ratio* over Japan generally corresponded well to the results of a previous analysis of observations (Fujita, 2013). However, compared with observations for Tokyo and Komae, the model simulation tended to underestimate *Ratio*. This was mainly caused by the local contribution of fine-mode NO_3^-. To improve the modeling reproducibility further, simulation at a finer resolution is required. For the Pacific Ocean, *Ratio* was above 0.7. The larger value of *Ratio* may be partly attributed to the amount of

wet deposition of coarse-mode NO_3^- because the deposition derived from long-range transport of fine-mode aerosols decreases over open oceans.

3.3. Sensitivity analysis for investigating factors that increase ratio

The modeling system used in this study was fully validated by comparison with observations across East Asia. Significantly increasing trends in observed *Ratio* were identified from the observation dataset for China (+9.8 ± 2.5%/year between 2006 and 2011), Korea (+13.2 ± 4.1%/year between 2006 and 2011), and Japan (+3.4 ± 1.0%/year between 2006 and 2011) (each $p < 0.05$ by Student's t-test). The increase was accompanied by an increase in the emission ratio of NOx/SO_2 in China, which we attributed to the large effect of anthropogenic emissions from China on precipitation chemistry over Japan. In 2005–2006, SO_2 emissions in China peaked and they have been declining since then, even though NOx emissions have been continuously rising. Consequently, an increase in both the NOx/SO_2 emission ratio and *Ratio* is expected. To investigate this more closely, a sensitivity analysis of the model simulation was conducted for 2009–2011, and the controlling factors in the increase of *Ratio* were examined.

The spatial distribution of *Ratio* is shown in Fig. 4(d), which is the average value for 2000–2011. *Ratio* over East Asia increased dramatically in 2006–2011; therefore, the spatial distribution of *Ratio* during 2000–2005 and 2006–2011 are illustrated in Fig. 5(a). The large increase from 2000–2005 to 2006–2011 was revealed by comparing these variations. Moreover, Fig. 5(b) shows the linear regression analysis for each period. During 2000–2005, the trend in *Ratio* is not clear. The increase of 5–10% around Japan stemmed from the eruption on Miyakejima in 2000. The large increase of nss-SO_4^{2-} concentration decreased *Ratio*, and the settling of the volcanic activity toward 2005 increased *Ratio*. In contrast, the trend for *Ratio* during 2006–2011 is clear above all regions in East Asia. The annual mean increase was near 10% above China (up to +15–20% in some areas) and Korea, and around 5% in Japan. The modeling results for this increase for *Ratio* corresponded well to the observations.

Finally, the controlling factors of the variations in *Ratio* are examined by two sensitivity simulations. Differences between *Ratio* of the estimated emissions case and fixed emission case averaged over 2009–2011 (Δ_{NS}) are described as

$$\Delta_{NS} = NO_3^-(\text{estimated case})\big/\text{nss-}SO_4^{2-}(\text{estimated case}) - NO_3^-(\text{fixed case})\big/\text{nss-}SO_4^{2-}(\text{fixed case}) \quad (2)$$

where the suffixes N and S indicate that both NO_3^- and nss-SO_4^{2-} concentration in precipitation were used for the estimated emissions case, and this is shown in Fig. 6(a). This clearly indicates that the increase of *Ratio* in the estimated case from the fixed emission case and the large increase (+0.20) of *Ratio* are found over eastern China and western Sea of Japan. Differences in *Ratio* between sensitivity simulations range from 0.05 to 0.15 above southern China and Korea, and from 0.00 to 0.10 above Japan. This increase in *Ratio* evaluated by the sensitivity simulation for the estimated emissions case during 2009–2011 corresponded well to the observed increase in *Ratio* from 2008 (Fig. 2). Note that the reproducibility of chemical components in precipitation and *Ratio* in precipitation decreased when the fixed emissions case was used for evaluation.

The variations in *Ratio* were mainly caused by the increase in NOx emissions from China and the decline in SO_2 emissions from China. To investigate which factors play a significant role in the increase of *Ratio* over East Asia, the effects of emission changes were analyzed. The relative contributions of NOx and SO_2 emission changes were investigated for two parameter settings: NO_3^- concentration in precipitation (estimated emissions case) with nss-SO_4^{2-} concentration in precipitation (fixed emissions case), and NO_3^- concentration in precipitation (fixed emission case) with nss-SO_4^{2-} concentration in precipitation (estimated emission case). These settings can be written in the same form as Eq. (1) as

$$\Delta_N = NO_3^-(\text{estimated case})\big/\text{nss-}SO_4^{2-}(\text{fixed case}) - NO_3^-(\text{fixed case})\big/\text{nss-}SO_4^{2-}(\text{fixed case}) \quad (3)$$

$$\Delta_S = NO_3^-(\text{fixed case})\big/\text{nss-}SO_4^{2-}(\text{estimated case}) - NO_3^-(\text{fixed case})\big/\text{nss-}SO_4^{2-}(\text{fixed case}) \quad (4)$$

These equations were used to investigate the effects of the changes in NOx and SO_2 emissions on *Ratio*. To evaluate the relative importance of changes in NOx and SO_2 emissions, their effects were normalized by using Δ_{NS}.

$$\text{Effect of } NO_x \text{ emission change} = \Delta_N/\Delta_{NS} \quad (5)$$

$$\text{Effect of } SO_2 \text{ emission change} = \Delta_S/\Delta_{NS} \quad (6)$$

The results are displayed in Fig. 6(b) and (c). The effects of emission changes in China on *Ratio* were different over East Asia. Above China, the effects of NOx emission increase in China was 55–60%; strong from the Asian continent to the Yellow Sea, the East China Sea, and western Japan (50–55%), and then it decreased above the Pacific Ocean (below 50%). In contrast, the effects of the decline in SO_2 emissions were smaller above China (below 40%), larger over eastern and northern Japan (35–45%), and much larger over the Pacific Ocean (above 50%). The sum of these contributions does not match the results of the estimated emissions case. This is partly because of the nonlinear production of NO_3^- through complex chemical reactions. The effects of the changes in the emissions presented in Fig. 6(b) and (c) were averaged for each country. In China, the effects of the increase in NOx emissions was 57.2% and

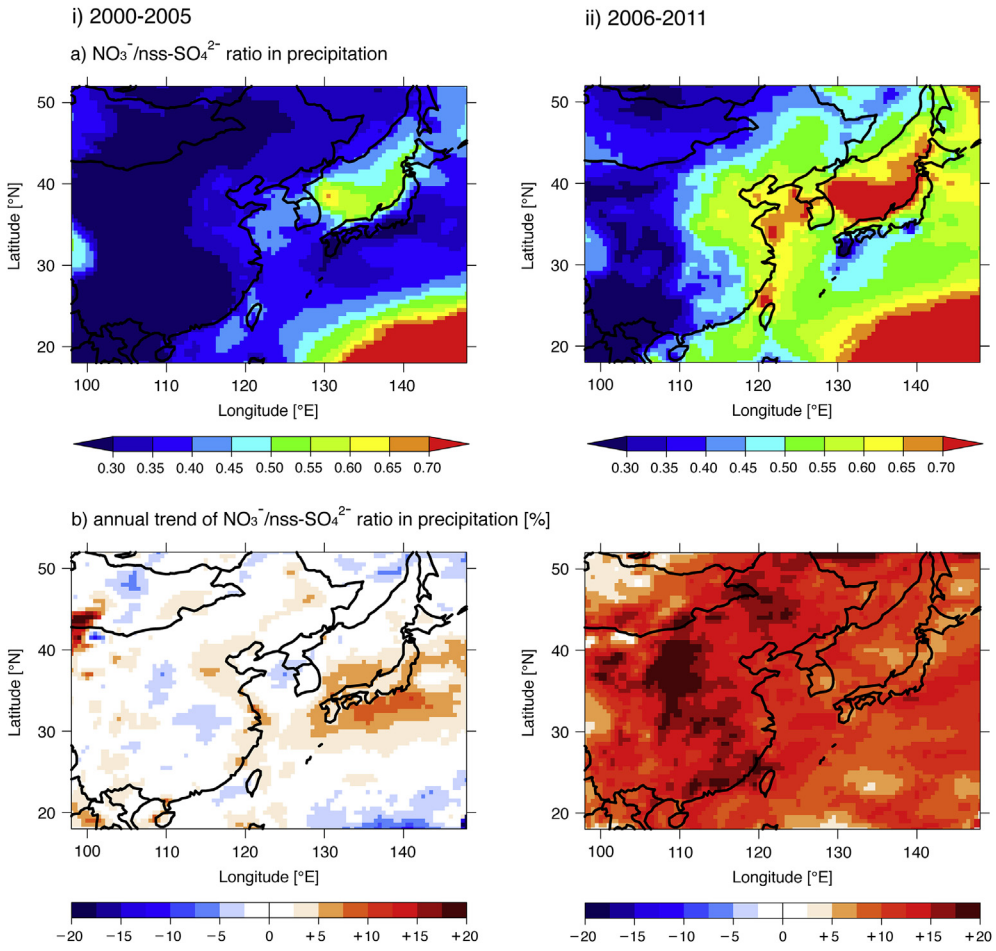


Fig. 5. (a) NO_3^-/nss-SO_4^{2-} ratio in precipitation averaged over (i) 2000–2005 and (ii) 2006–2011; (b) Annual trend of NO_3^-/nss-SO_4^{2-} ratio in precipitation by linear regression analysis in (i) 2000–2005 and (ii) 2006–2011.

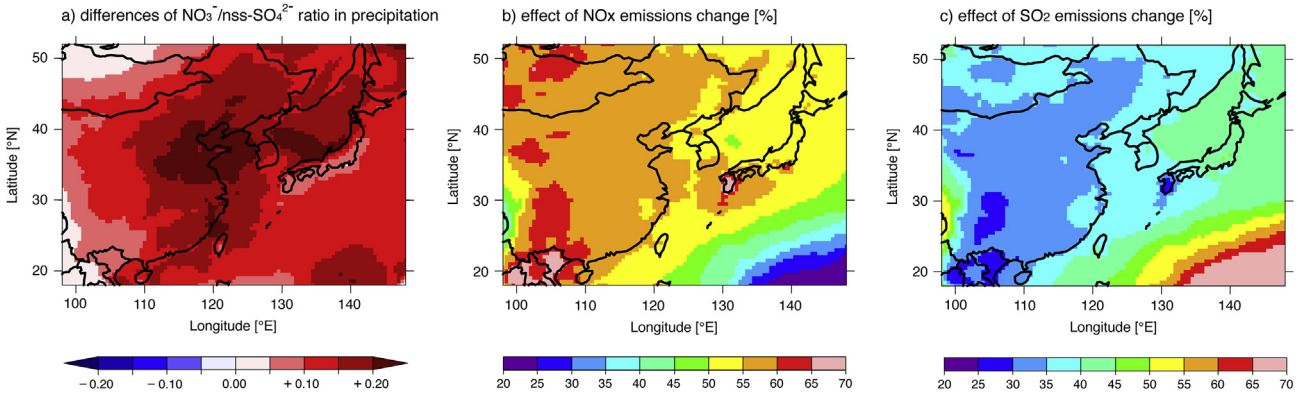


Fig. 6. (a) Changes in NO_3^-/nss-SO_4^{2-} ratio in precipitation averaged over 2009–2011 from the model simulation with the fixed emission case for the model simulation and the estimated emission case (Δ_{NS}). Effect on variation in NO_3^-/nss-SO_4^{2-} ratio in precipitation caused by (b) NOx emission changes in China, and (c) SO_2 emission changes in China.

the decline in SO_2 emissions was 33.9%, in Korea, they were 54.8% and 38.2%, and in Japan they were 54.3% and 39.8%. In our previous study, we concluded that an increase in NOx emissions from China and a decline in SO_2 emissions from China played equally important roles in increasing *Ratio* over Japan. The increase of NOx emissions and decline of SO_2 emissions contributed 50% and 45%, respectively, to the increase in *Ratio* (Itahashi et al., 2014a, Table 3). The differences in the effects of the emission changes were caused by the estimated emissions in 2011. In 2011, NOx emissions expanded further from 2010, whereas the SO_2 emissions used were the same as in 2010; therefore, the effect of NOx emissions changes are much larger in 2011.

4. Concluding remarks

The variations in precipitation chemistry were analyzed

between 2000 and 2011, focusing on the behavior of *Ratio*, which is defined as NO_3^-/nss-SO_4^{2-} concentration in precipitation. The emissions trend over China, where NOx emissions have been continuously increasing and SO_2 emissions have been decreasing since 2005–2006, have a substantial effect on precipitation chemistry over East Asia. In our previous study (Itahashi et al., 2014a), we found that an increase in NOx emissions and a decline in SO_2 emissions from China contributed almost equally to the increase in *Ratio* over Japan. We applied this approach to precipitation chemistry above China and Korea, and further extended the analysis period to 2011. *Ratio* above China, Korea, and Japan showed a slight decrease or no change between 2000 and 2005, and subsequently increased from 2006 to 2011. The linear increases during 2006–2011 were significant, at +3.4 ± 1.0%/year in Japan, +13.2 ± 4.1%/year in Korea, and +9.8 ± 2.5%/year in China (each $p < 0.05$). The changes in *Ratio* corresponded well to the changes in the NOx/SO_2 emission ratio from China but not from Korea and Japan. To investigate the effect of emission changes in China further, we conducted a model simulation with a sensitivity simulation. Our modeling system captured the observed precipitation, NO_3^- and nss-SO_4^{2-} concentration in precipitation, and *Ratio* in precipitation for 2000–2011. Two sensitivity simulations were conducted for 2009, 2010, and 2011 with 1) fixed emissions in 2008 and 2) estimated Chinese emissions with the constraint of the satellite observation data. This analysis clarified that the increase in NOx emissions from China was responsible for 55–60% of the effects on *Ratio* above China and 50–55% for Korea to Japan. The effect of the decline in SO_2 emissions from China had a larger contribution to the downwind region of China with less than 40% in China and 35–45% in Korea and Japan. The behavior of *Ratio* and the acidifying species in precipitation over East Asia should be monitored because high anthropogenic emissions are an ongoing problem. The observation data in this study is limited in southern China; hence, the analysis above northern China is necessary for evaluating the behavior of precipitation chemistry in China further. In addition, several previous simulation studies have described the discrepancies of the contribution of China to downwind regions (e.g., Ge et al., 2014); therefore, the comparison of studies, especially for emissions, is needed to reduce the uncertainty.

Acknowledgments

The authors thank EANET and JMA for collecting and providing wet deposition measurement data. We are grateful to the three anonymous reviewers for their constructive comment.

References

Akimoto, H., 2003. Global air quality and pollution. Science 302 (1716), 1716–1719.
Byun, D.W., Schere, K.L., 2006. Review of the governing equations, computational algorithms, and other components of the model-3 community multiscale air quality (CMAQ) modeling system. Appl. Mech. Rev. 59, 51–77.
EANET, 2000a. Technical Manual for Wet Deposition Monitoring in East Asia. http://www.eanet.asia/product/manual/prev/techwet.pdf.
EANET, 2000b. Quality Assurance/Quality Control (QA/QC) Program for Wet Deposition Monitoring in East Asia. http://www.eanet.asia/product/qaqc/qaqcwet.pdf.
Fujita, S., Takahashi, A., Weng, J.-H., Huang, L.-F., Kim, H.-K., Li, C.-K., Huang, F.T.C., Jeng, F.-T., 2000. Precipitation chemistry in East Asia. Atmos. Environ. 34, 525–537.
Fujita, S., Takahashi, A., Sakurai, T., 2003. The wet deposition of acid and some major ions over the Japanese archipelago. Tellus 55B, 23–34.
Fujita, S., 2013. Long-term trends in the nitrate to non-sea-salt sulfate ratio in precipitation over the Japanese archipelago. J. Jpn. Soc. Atmos. Environ. 12–19 (Japanese with English abstract).
Ge, B.Z., Wang, Z.F., Xu, X.B., Wu, J.B., Yu, X.L., Li, J., 2014. Wet deposition of acidifying substances in different regions of China and the rest of East Asia: modeling with updated NAQPMS. Environ. Pollut. 187, 10–21.
Itahashi, S., Uno, I., Yumimoto, K., Irie, H., Osada, K., Ogata, K., Fukushima, H., Wang, Z., Ohara, T., 2012. Interannual variation in the fine-mode MODIS aerosol optical depth and its relationship to the changes in sulfur dioxide emissions in China between 2000 and 2010. Atmos. Chem. Phys. 12, 2631–2640.
Itahashi, S., Uno, I., Hayami, H., Fujita, S., 2014a. Modeling investigation of controlling factors in the increasing ratio of nitrate to non-seasalt sulfate in precipitation over Japan. Atmos. Environ. 92, 171–177.
Itahashi, S., Uno, I., Irie, H., Kurokawa, J., Ohara, T., 2014b. Regional modeling of tropospheric NO_2 vertical column density over East Asia during the period 2000–2010: comparison with multisatellite observations. Atmos. Chem. Phys. 14, 3623–3635.
Kurokawa, J., Ohara, T., Morikawa, T., Hanayama, S., Greet, J.-M., Fukui, T., Kawashima, K., Akimoto, H., 2013. Emissions of air pollutants and greenhouse gases over Asian regions during 2000–2008: regional emission inventory in Asia (REAS) version 2. Atmos. Chem. Phys. 13, 11019–11058.
Takahashi, A., Fujita, S., 2000. Long-term trends in nitrate to non-seasalt sulfate ratio in precipitation collected in western Japan. Atmos. Environ. 34, 4551–4555.
U.S. NAPAP (National Acid Precipitation Assessment Program), 1991. The U.S. National Acid Precipitation Program, vol. I.. U.S. Government Printing Office, Washington, DC.